PEERING INTO THE FORMATION AND DEVITRIFICATION OF METALLIC GLASSES

Metallic glasses are an important class of materials, because of their many unique properties and because their devitrification characteristics can reveal a great deal about how the formation of such materials may be controlled. Devitrification involves gradually heating a metallic glass until thermal energy becomes sufficient to allow for atomic realignments into a more ordered crystalline state. Controlling devitrification is important, for example, to the formation of nanoscale materials, such as rare-earth permanent magnets, which are often produced by rapidly solidifying and heat treating amorphous alloys to obtain optimal magnetic properties.

Researchers from Ames Laboratory and Argonne National Laboratory used high-temperature x-ray diffraction (HTXRD) to investigate the devitrification pathways of two related zirconium-based metallic glasses: $Zr_{70}Pd_{30}$ and $Zr_{70}Pd_{20}Cu_{10}$. Charges of $Zr_{70}Pd_{30}$ and $Zr_{70}Pd_{20}Cu_{10}$ were inductively melted to about 1500K and ejected onto a Cu wheel rotating at a tangential wheel speed of 25 m/s. Long, continuous ribbons of very uniform thickness (0.03 mm) and width (2 mm) were produced and cut into ~8-mm lengths for HTXRD measurements at the APS.

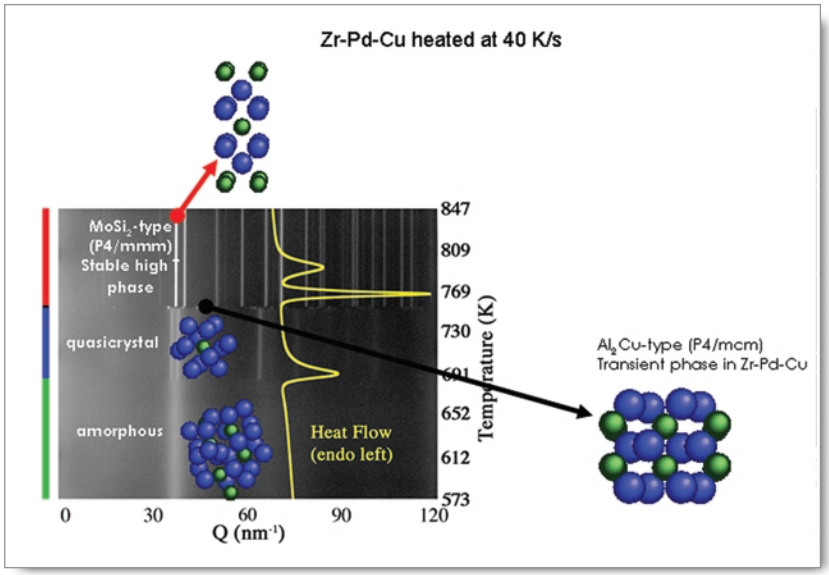

Fig. 1 The $Zr_{70}Pd_{20}Cu_{10}$ alloy shows a rapid transition from the icosahedral phase to the Al_2Cu-type structure, which undergoes a polymorphic transition to the $MoSi_2$-type structure at high temperature.

Time-resolved synchrotron x-ray studies were performed using energies of 80.73 and 124.63 keV at the XOR 1-ID-C and MU-CAT 6-ID-D beamlines, respectively. Thermal analysis was conducted on as-quenched samples to assess heats of formation and nucleation kinetics, by using differential scanning calorimetry at scanning rates of 5–40°C/min.

The studies demonstrated that the $Zr_{70}Pd_{30}$ and $Zr_{70}Pd_{20}Cu_{10}$ alloys have similar as-quenched structures and show a transition from the amorphous to an icosahedral phase over a narrow temperature range, the onset temperature for the $ZZr_{70}Pd_{30}$ alloy being about 30 K higher than that for $Zr_{70}Pd_{20}Cu_{10}$. Isothermal HTXRD suggests that devitrification occurs by nucleation and growth of the icosahedral phase. The $Zr_{70}Pd_{20}Cu_{10}$ alloy shows a rapid transition from the icosahedral phase to the Al_2Cu-type structure and then undergoes a polymorphic transition to the $MoSi_2$-type structure, which is the stable phase at high temperature (Fig. 1). The $Zr_{70}Pd_{30}$ alloy clearly shows coexistence of the quasicrystalline and $MoSi_2$-type structures.

While many transition metal alloys can be quenched to form amorphous alloys, few form icosahedral phases during devitrification. The Zr-based alloys are interesting because many compositions form icosahedral order during devitrification from the glass phase. To establish if there exists any relationship between the structure of the liquid and icosahedral order in the solid, a number of questions need to be addressed: What is the short-range order (SRO) of the as-quenched alloy, and how is it altered by the starting chemistry? What role, if any, does the SRO have on the devitrification products, particularly the formation of the icosahedral phase? Moreover, how does composition affect the stability of the icosahedral phase and subsequent crystallization pathways?

This study shows that HTXRD, using high-energy synchrotron radiation, is a promising tool for helping to answer these questions, since it provides high signal-to-noise diffraction data over a long reciprocal distance with collection times having the same timescale as the reaction kinetics. Because of their excellent signal-to-noise characteristics over short counting times and high spatial resolution, the high-flux high-energy photons derived from third-generation synchrotron sources, such as the APS, are ideal for studying the SRO of metallic glasses and the nanoscale structures formed during devitrification. ❍

See: M.J. Kramer[1], M.F. Besser[1], N. Yang[1], E. Rozhkova[1], D.J. Sordelet[1], Y. Zhang[2], and P.L. Lee[2], "Devitrification studies of Zr–Pd and Zr–Pd–Cu metallic glasses," J. Non-Cryst. Solids 317, 62–70 (2003).

Author affiliations: [1]Iowa State University, [2]Argonne National Laboratory

The MU-CAT sector at the APS is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, through the Ames Laboratory under Contract No. W-7405-Eng-82. Use of the APS and XOR was supported by the U.S. Department of Energy, Officece of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

INELASTIC X-RAY SCATTERING MEASUREMENTS AND *AB INITIO* DENSITY-RESPONSE CALCULATIONS REVEAL MANY-BODY ELECTRONIC CORRELATIONS

Electron-electron interactions play a central role in determining the physical properties of materials, including all transport-related phenomena. Although short-range exchange-correlation effects have long been studied theoretically, a full description of them with regard to solids remains a significant challenge. Fortunately, the availability of third-generation synchrotron sources and high-resolution inelastic-scattering facilities now permits detailed experimental investigations of large wave-vector processes associated with short-range many-body effects in materials with relatively high and low atomic number. This new experimental capability has emerged concurrently with advances in *ab initio* electron density-response calculation methods for periodic crystals. The confluence of these developments has enabled the exploitation of the direct, absolute intensity linkage between dynamical electronic response calculations and inelastic x-ray scattering (IXS) spectra through the dynamical structure factor, yielding a means of achieving a fundamental understanding of electron correlations.

Researchers from Oak Ridge National Laboratory, the University of Illinois at Urbana-Champaign, Universität Würzburg, and the University of Tennessee have shown that the dynamical structure factor per unit volume (rather than per unit cell) provides a natural connection to first-principles density-response calculations, including all-electron methods. They used pseudo-potential dynamical response calculations make it possible to augment first-moment absolute normalizations beyond semi-core absorption edges for *f*-sum rule evaluations in free-electron materials. In addition, a method was provided for transferring absolute IXS calibrations to arbitrary materials, such as the transition-metal oxides, as part of a fundamental investigation of dynamical electronic correlations in aluminum.

Figure 1 shows measurements, made on the UNI-CAT ID-33 beamline at the APS, that were used in connection with a theoretical extension of first-moment intensity determinations for free electrons beyond the 72-eV semi-core absorption edge in aluminum. This procedure provided an accurate, absolute normalization for dynamical structure factor measurements made at the Fermi wave vector, k_F, in aluminum, which was used to analyze IXS measurements performed on ⟨001⟩- and ⟨013⟩-oriented aluminum single crystals on the X-21 beamline at the National Synchrotron Light Source. Quantitative evaluation of the measurements was carried with *ab initio*, time-dependent density-functional theory (TDDFT) calculations of electron-hole excitation spectra that included the band structure and many-body kernels based on the local-density approximation and dynamical exchange decoupling techniques. Dynamical electronic response calculations of the dynamical structure factor made using the many-body kernel obtained within the adiabatic extension of the local-density approximation (ALDA) yielded good agreement with the IXS energy-loss spectra for energies up to about 30 eV and momentum transfers up to k_F. For energy losses above 15 eV, the complex, frequency-dependent, dynamical exchange decoupling-based many-body kernel of Devreese et al. [1] was shown to lead to a description of the IXS data that was comparable or better than that provided by the ALDA. For low energies, though, the ALDA worked better, presumably because of the absence of correlations in the dynamical exchange kernel.

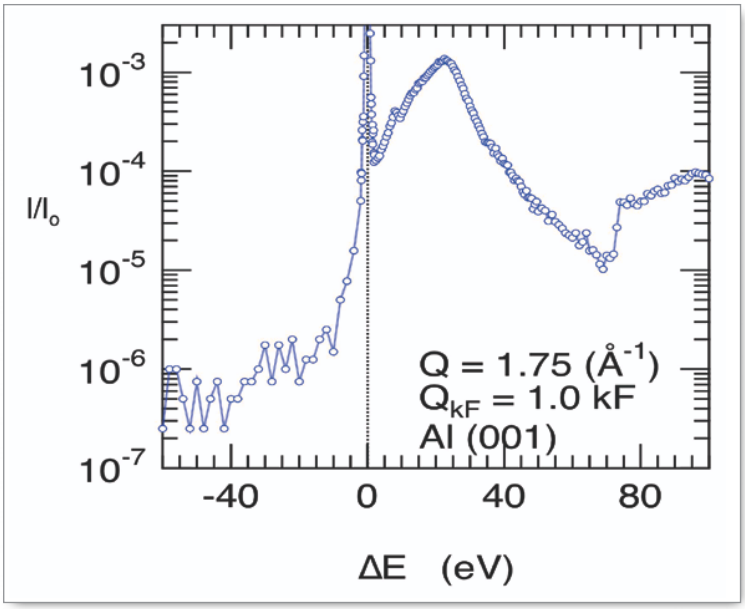

Fig. 1. Logarithmic-scale plot of the IXS measured energy-loss spectrum at the Fermi wave vector, k_F, in the [001] direction in Al. Measurements at negative ΔE provide an estimate of the background for corresponding positive ΔE values, indicating that first moment *f* sum-rule integrations for free electrons must be extended beyond the 72-eV L-absorption edge using theoretical response calculations.

The work provides a general method for the absolute calibration of IXS measurements on arbitrary materials. It suggests that high-precision IXS measurements, in combination with state-of-the-art TDDFT calculations for periodic crystals, offer a promising framework for benchmark development toward the goal of fundamental treatments of dynamical correlations in real materials. ❍

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X-ray-Induced Fluorescence Enables Detailed Study of High-pressure Arc Plasmas

Metal-halide arc lamps are among the most energy-efficient sources of white light, which is why they are frequently used to illuminate large stadiums, malls, warehouses, and roadways. With further improvements in efficiency, produced by scientific and engineering advances, they could also see use in applications currently dominated by fluorescent and incandescent lamps.

A typical metal-halide arc lamp consists of a sealed evacuated tube containing two electrodes, several milligrams of Hg, smaller amounts of argon and various metal-halide salts. When a sufficient electrical potential is placed between the electrodes, an argon glow discharge is initially ignited. As the tube heats up, Hg evaporates, raising the pressure in the tube. At sufficiently high pressures, the discharge transitions from a glow to an arc. Further heating causes the metal-halide salts to evaporate and then dissociate as they move into the arc. The resulting free metal atoms and their ions become the most important source of visible light.

The plasma arcs responsible for visible light production by metal-halide lamps pose a daunting challenge to researchers seeking to observe and understand phenomena occurring in these arcs. Besides being chemically complex, metal-halide lighting arcs are opaque in many portions of the optical spectrum, hindering traditional optical diagnostics. The tubes encasing the arcs also scatter optical wavelengths, even when the tubes are transparent. This limitation has become more severe with the recent introduction of high-temperature polycrystalline alumina (PCA) arc tubes, which are translucent instead of transparent. Optical emission by the arc is also scattered strongly by PCA. Such scattering effectively negates any attempt at determining spatially resolved distributions of the contributing atoms, ions, and molecules.

It has long been recognized that the technique of x-ray-induced fluorescence could overcome these difficulties because x-rays are virtually unaffected by arc opacity or arc-tube scattering. Although this technique was initially tried elsewhere, it was first demonstrated successfully in arc lamps at the XOR 1-ID beamline at the APS, because of the beamline's high-energy, high-brightness, and monochromatic radiation, all of which are necessary to make x-ray-induced fluorescence practical for measurements in high-pressure metal-halide arcs.

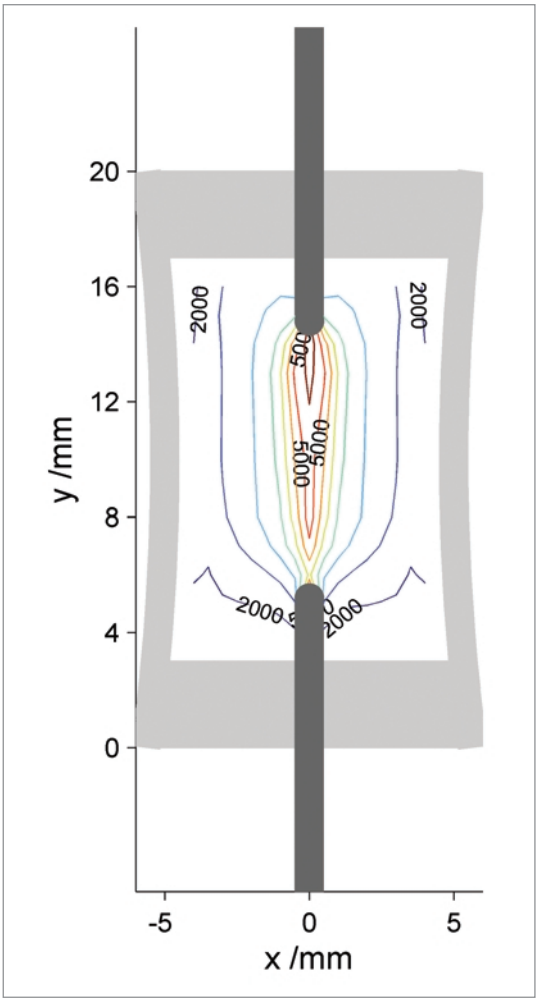

Fig. 1. Temperature contours in a 150 W ceramic metal-halide lamp containing a Hg/DyI_3/CsI mixture. Temperature values are in Kelvin with contours separated by 500K. The light gray regions represent the translucent ceramic arc tube, and the dark gray regions represent tungsten electrodes.

In x-ray-induced fluorescence, high-energy synchrotron radiation induces K-shell fluorescence in the components of a high-pressure plasma arc. The detected fluorescence is spectrally resolved, so that multiple elemental species are observed simultaneously. The penetrating nature of the high-energy photons allowed researchers from the National Institute of Standards and Technology, OSRAM SYLVANIA, and Argonne National Laboratory to make these measurements *in situ*, while the arc remained contained by an optically translucent PCA arc tube and a glass vacuum jacket. Absolute densities of Hg, the metal additives, and iodine were measured with an absolute calibration obtained by comparison with observed fluorescence from cells containing a known density of Dy in solution.

The gas density, equivalent to the Hg density (along with a knowledge of the lamp pressure), allowed the researchers to establish the gas temperature distribution in the arc (Fig. 1). The elemental densities and gas temperature then allowed them to derive the distributions of light-emitting and light-absorbing atomic and molecular species in the arc. Spatial distributions extending from one end of the arc tube to the other and from the arc core all the way to the wall were obtained for all of the principal elements in the arc (Fig. 2). These parameters are essential to developing a clearer scientific understanding of these high-pressure arc systems, and they cannot be obtained in any other way.

In the experiment, the arc saw a millimeter-size beam of monochromatic x-rays, the energy of which was tuned in the range of 70 to 85 keV, depending on the species to be observed. The energy resolution was ~1 part in 10^3, and photon flux densities were on the order of 10^{12} s^{-1} mm^{-2}.

Besides being useful for research into high-pressure lighting arcs, the technique of x-ray-induced fluorescence could also be applied to the study of a variety of other arc plasma systems, including arcs without arc-tube enclosures and arcs that must be accessed through an x-ray window. ❍

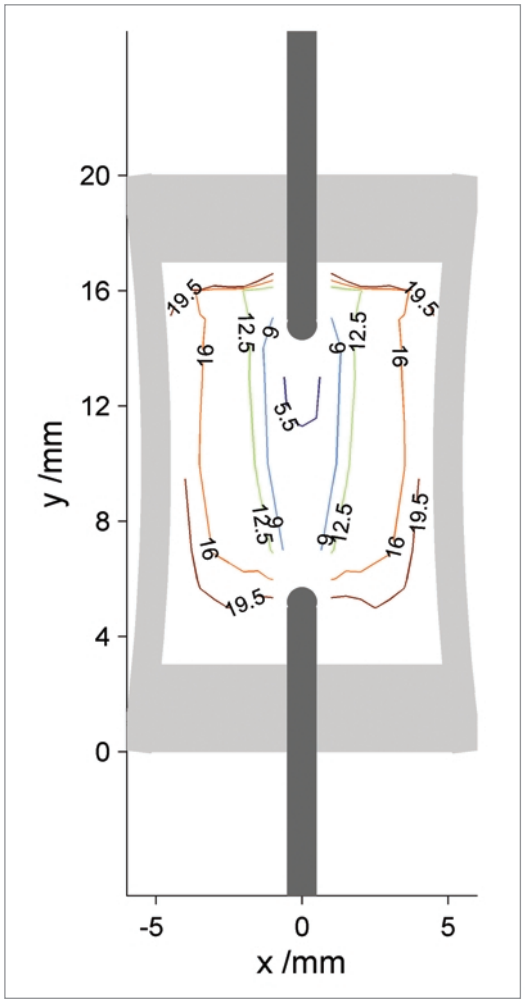

Fig. 2. Dy density contours in a 150-W ceramic metal-halide lamp containing a $Hg/DyI_3/CsI$ mixture. Density values are in 10^{16} cm^{-3} with contours separated by 3.5 x 10^{16} cm^{-3}. Dy produces most of the visible light emitted by the arc. These contours represent the total elemental Dy densities. The light gray regions represent the translucent ceramic arc tube, and the dark gray regions represent tungsten electrodes.

See: J.J. Curry [1], H.G. Adler [2], S.D. Shastri [3], and W.-K. Lee [3], "X-ray induced fluorescence measurement of density distributions in a metal–halide lighting arc," J. Appl. Phys. **93**(5), 2359-2368 (1 March 2003).

Author affiliations: [1]National Institute of Standards and Technology, [2]OSRAM SYLVANIA, [3]Argonne National Laboratory

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TWO GROWTH MODES FOR OXIDE FILMS ON TEXTURED METAL SUBSTRATES

Most crystalline materials are composed of small single-crystal grains that are packed together to form complicated networks of phase and grain boundaries. Although local three-dimensional grain-by-grain interactions ultimately determine the structural and electronic behavior of such materials, these interactions have long been virtually impossible to observe directly. Thanks, however, to enormous increases in x-ray brilliance provided by third-generation synchrotron sources and advances in x-ray mirrors, Fresnel zone plates, and refractive lenses, x-ray microbeam studies of individual grains in polycrystalline matrices can now simultaneously characterize the local structure, orientation, and strain tensor of different heteroepitaxial layers with submicrometer resolution in three dimensions.

These capabilities were demonstrated by researchers from Oak Ridge National Laboratory, the Advanced Light Source, the University of Florida, Soongsil University, and the Korea Electrotechnology Research Institute. The measurements were performed at the UNI-CAT 34-ID and MHATT/XOR 7-ID beamlines at the APS.

The researchers used polychromatic synchrotron radiation in an investigation of the epitaxial growth of cerium oxide (CeO_2) films on textured nickel (Ni) substrates deposited by pulsed laser deposition. Understanding the microstructure of these and similar materials is crucial to the development of deposited-superconductor technology. The focused polychromatic beam was diffracted from a submicrometer-diameter area within a single grain of the CeO_2/Ni sample, producing complete diffraction patterns from each layer on a charge-coupled-device area detector. Quantitative analysis of the Laue patterns yielded the local lattice orientation (resolution ~0.01°) and deviatoric strain tensor (resolution ~10^{-4}) for each layer.

Grain-by-grain microstructural studies of the cerium oxide films revealed two distinct kinetic growth regimes: ledge growth at elevated temperatures and island growth at lower temperatures. In addition, a combinatorial approach showed that crystallographic tilting associated with these complex interfaces is qualitatively described by a simple geometrical model applicable to brittle films on ductile substrates.

As indicated in Fig. 1, large-area orientation mapping also revealed that the tilting gave rise to enhanced texture and thus greater percolation distances in the oxide film. With regard to practical applications, these results suggest that significant enhancements can be achieved in heteroepitaxial systems with large lattice mismatch, in contrast to conventional growth approaches where lattice mismatch is typically minimized.

The tilt mechanisms studied should be relevant to many oxide/metal systems, including thermal barrier coatings, solar cells, and corrosion and interfaces in electronic devices. Thus, the benefits of intentionally enhanced texture should be achievable for many coated materials. Additional experiments examining more localized microstructures, such as grain-boundary grooves and crack propagation, are now possible with microbeams, and are in progress. ❍

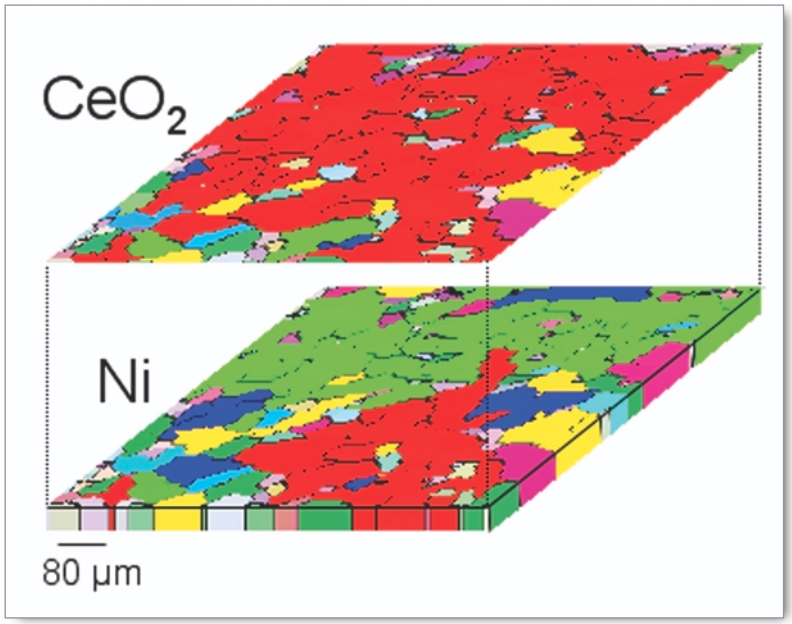

Fig. 1. Orientation maps from a deposited oxide film and a textured Ni substrate obtained by using x-ray Laue microdiffraction. Black lines within each map indicate boundaries where the total misorientation is greater than 5°. Each colored area shows a percolative region connected by boundaries of less than 5°. The oxide film exhibits larger percolation distances than the substrate, due to crystallographic tilts induced during epitaxial growth.

See: J.D. Budai[1], W. Yang[1], N. Tamura[2], J.-S. Chung[3], J.Z. Tischler[1], B.C. Larson[1], G.E. Ice[1], C. Park[4], and D.P. Norton[5], "X-ray microdiffraction study of growth modes and crystallographic tilts in oxide films on metal substrates," Nat. Mater. **2**, 487-492 (July 2003).

Author affiliations: [1]Oak Ridge National Laboratory, [2]Lawrence Berkeley National Laboratory, [3]Soongsil University, [4]Korea Electrotechnology Research Institute, [5]University of Florida

This research was sponsored by the U.S. Department of Energy Office of Basic Energy Sciences, Division of Materials Sciences, under contract with Oak Ridge National Laboratory, managed by UT-Battelle, LLC. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.